

Sea-salt Aerosol Surfaces

New Synchrotron Photoelectron Spectroscopy Technique Probes Liquid Surfaces

Using a unique x-ray photoelectron spectroscopy system that allows the study of surfaces in their natural environment—at almost normal pressures and in the presence of water vapor—an MSD group led by Miquel Salmeron has shown that negatively charged anions concentrate at the surface of salted droplets of water.

Sea salt droplets in the atmosphere result from ocean waves and wind action. The structure and composition of their surface and their interaction with environmental gases such as chlorofluorocarbons is key to understanding their role in catalyzing ozone depletion reactions. Atmospheric chemists are particularly interested in knowing how cations and anions in these salted droplets arrange themselves near the droplet surface. Theoretical models predict and indirect observations suggest, that the surface is enriched in anions, the more so the larger the anion (I more than Br, Br more than Cl). Unfortunately none of the existing x-ray based spectroscopic techniques can provide a direct measurement of this because they require that the material be placed in a vacuum, where the study of liquid surfaces is impossible.

The LBNL team has developed novel ambient pressure x-ray photoelectron spectroscopy instruments at ALS beamlines 9.3.2 and 11.0.2. Like all photoelectron spectroscopy systems, they identify elements at surfaces, by detecting their unique spectral signals. But unlike other such systems, they can do this under environmentally relevant temperature, pressure and humidity. The ALS is one of only two places in the world where photoelectron spectroscopy can be performed on surfaces at pressures above 1 torr (1 millimeter of mercury in a barometer). The other such instrument is at the Berlin Electron Storage Ring Company for Synchrotron Radiation (BESSY) in Berlin, Germany.

The first generation system, at beamline 9.3.2, was used to explore the premelting of ice, i.e., the formation of a liquid layer at the ice surface at a temperature close to but below the actual melting point (MSD Highlight 02-5). The new study involved the study of salt grains as they dissolve when exposed to water vapor. The team placed two different types of salt grains (potassium bromide and potassium iodide) in the vacuum chamber of the high-pressure spectroscopy system and slowly increased the humidity. At first, a thin film of water developed on the grains. When the vapor pressure was high enough, the grains liquefied (deliquesce). For the first time, the instrument enabled the team to spectroscopically chronicle the behavior of the ions from the moment water condenses on the surfaces of the grains until after the grains dissolve. They found that in both cases positively charged potassium ions sank under a few molecular layers of the film of water, while the negatively charged iodine and bromine ions rose to the surface. In comparing the two salts, it was found the enhancement of anion concentration was more dramatic for the larger, more polarizable iodide anion. These results, and additional depth-resolved measurements, are in agreement with theoretical models.

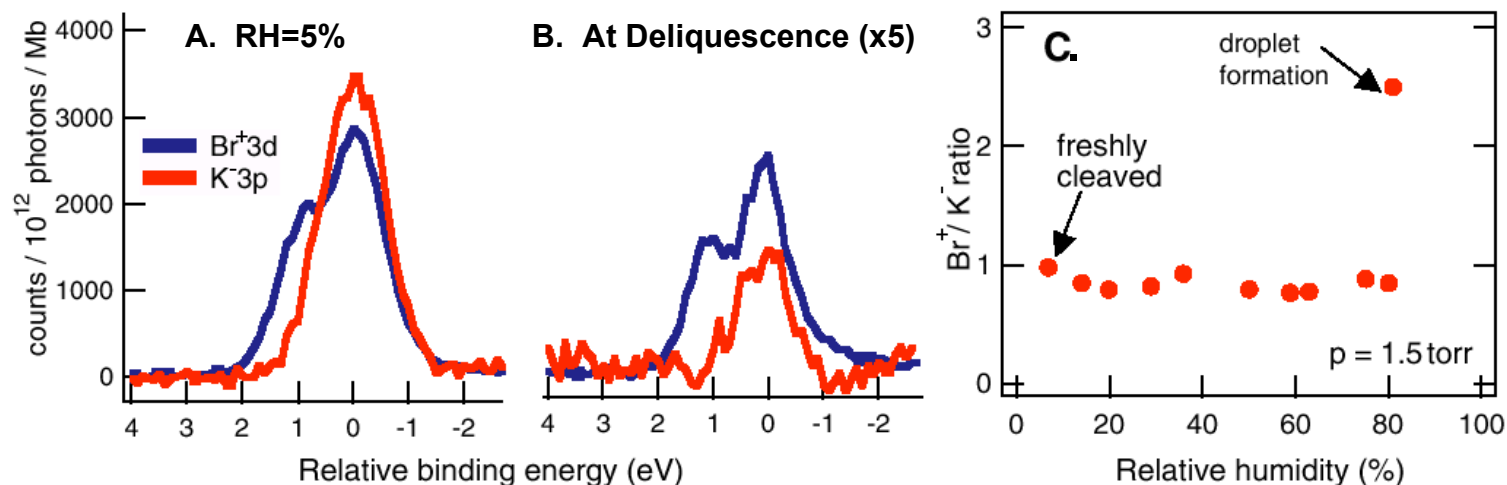
Now, Salmeron and his team plan to add other gases such as chlorofluorocarbons to the system to elucidate the role of sea salts in ozone destruction. They also plan to examine how humidity affects the surface of other materials, including organic compounds, to study the structure of water in contact with biomaterials, and also inorganic materials, such as soil minerals, and silicon.

M. Salmeron (510) 486-6230, Materials Sciences Division (510) 486-6230, Berkeley Lab.

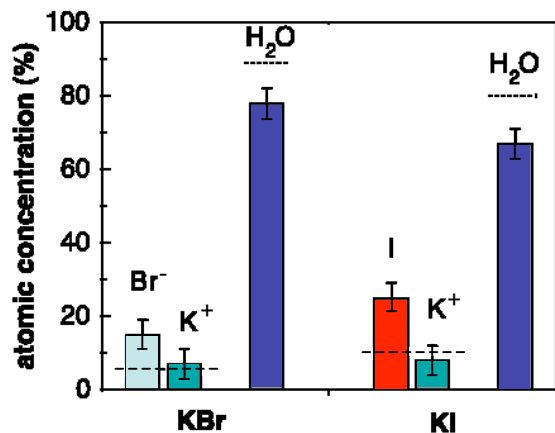
S. Ghosal, J. C. Hemminger, H. Bluhm, B. S. Mun, E. L. D. Hebenstreit, G. Ketteler, D. F. Ogletree, F. G. Requejo, and M. Salmeron, "Electron Spectroscopy of Aqueous Solution Interfaces Reveals Surface Enhancement of Halides," *Science* **307**, 563 (2005).

Sea-Salt Aerosol Surfaces

New Synchrotron Spectroscopy Technique Probes Solution Dynamics



High pressure x-ray photoelectron spectra provide a direct determination of the concentration of anions and cations at the surface of salt in aqueous solutions. When KBr crystals are exposed to increasing humidity, the Br/K^+ ratio at the surface remains virtually constant until the deliquescence point (when the crystal dissolves) is reached. Then the signal from the bromine anion (blue) increases compared to the potassium cation (red).



Atomic concentrations in the first two to three atomic layers of the saturated water/salt solution that forms on top of the crystals at the deliquescence point. The dashed lines indicate expected concentrations of ions and water molecules from thermodynamic data for bulk, saturated solutions. The surface enhancement of the anion concentration is more dramatic for the larger, more polarizable iodide anion.